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BIDISPERSE FERROFLUIDS WITH CHAIN AGGREGATES: MICROSTRUCTURE AND MACROSCOPIC PROPERTIES

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Ferrofluids can be viewed as particular interesting class of dipolar fluids, which have a wide range of potential application in biomedicine and technology and in this report the research of a bidisperse ferrofluids with chain aggregates are presented. A novel theoretical approach was developed to describe the microstructure and macroscopic properties of such systems. It was shown the presence of chains leads to an increase of the initial susceptibility in comparison with that of a homogeneous ferrocolloid. The behaviour of the structure factor in the region of the first peak and in the region of large wave vectors is studied in detail, and related to the observed microstructure. Obtained results demonstrate that the combined method developed is suitable for revealing the connection between microstructure and scattering images, and thus can help to interpret experimental results such as small angle neutron scattering images.

This research was started in 2005 and connected with magnetic fluids (MF). They are colloidal systems consisting of particles (magnetic particles, ferroparticles) suspended in magneto-passive liquids. The external magnetic field can orient the ferroparticle magnetic moments, which leads to the change of MF properties, such as viscosity, phase behavior, or their optical birefringence. Their unique combination of strong response to the external magnetic field with their liquid state gives rise to numerous applications of magnetic fluids in engineering and arts, and the magnetic fluids appear to be very useful in biomedical applications as an effective tool in cancer treatment.

The most typical microstructural aggregates for magnetic fluids are the chains of magnetic particles. The existence of fractal loose aggregates and drops is also possible. Formation of different structures can lead to significant changes in different properties of ferrofluids, therefore, active investigations are carried out in this field. The bidisperse model is the first approximation of real ferrofluids, in which the particles have different sizes. It is extremely important to consider the polydispersity in theoretical descriptions of aggregate formation in magnetic fluids. Additionally, the influence of the external magnetic field has to be considered when the processes of aggregate formation in ferrofluids are studied.

In this research work I have developed a theoretical model, which describes the formation of flexible chains in bidisperse magnetic fluids under the influence of an arbitrary valued external magnetic field. This model is based on the Density Functional Theory (DFT). Afterwards, the results of the theoretical approach and the computer simulation data were compared [1]. A very good qualitative and, what is important, quantitative agreement between the theoretical and the simulation results on magnetization and initial susceptibility has been obtained for all samples. It has been shown that the presence of chains influences significantly the magnetic properties of ferrofluids. The external magnetic field stimulates the process of chains formation. Structure analysis has also resulted in a complete qualitative and quantitative agreement between the theoretical model and the computer simulation.

To summarize my theoretical results I got rid of the major part of the approximations usually adopted in theoretical models dealing with the chain formation in ferrofluids. I used a bidisperse model ferrofluid with flexible chains under the influence of an arbitrary valued external magnetic field and compared the results with the data obtained via simulations of the fully interacting fluid. A novel theoretical approach has been developed to describe the magnetostatic properties of the bidisperse model ferrofluid with chain aggregates. The chain partition function was calculated analytically allowing for the chain flexibility in an arbitrary valued external magnetic field. The presence of chains leads to an increase of the initial susceptibility if compared to that of homogeneous ferrofluids. I have successfully described this susceptibility growth, which was found in computer simulations in binary model ferrofluids with different granulometric compositions in terms of the developed approach. The chain flexibility, which was taken into account in this approach, allowed me to get a convincing quantitative agreement between the theoretically and numerically obtained magnetization curves and the initial susceptibility for different granulometric compositions of the model fluid. However, a deeper analysis of the cluster structure has shown noticeable deviations in cluster sizes and distributions. This occurs due to the use of different energy cluster criteria for the cluster analysis. The energy criterion used to analyze the simulations could not be used in the same way in the theoretical approach, and vice versa, due to technical problems. Nevertheless, I have found a convincing agreement between the simulation and the theoretical results for the qualitative (relative) behaviour of microstructural observables for different model binary ferrofluids. The deviations in cluster analysis were not qualitative, but they were caused by the difference in the applied cluster criterion. To verify this assumption I carried out an extensive theoretical and numerical cluster analysis using the same entropic cluster definition. I have got a full qualitative and quantitative agreement between simulation and theoretical microstructural observables. Another important conclusion is the following: the nearest neighbour limitation and the neglect of inter chain interaction, which are still present in theory, compensate each other in the region of the investigated parameters of my systems. Unfortunately, the entropy criterion cannot be used for theoretical description of the ferrofluid macroscopic properties, because, according to this criterion, even slightly correlated particles, which occasionally appear to be close to each other, are treated as a new kinetic stable unit, resulting in a considerable overestimation of the number of clusters, and, as a consequence, this results in wrong macroscopic observables. However, one should keep in mind that an analysis of entropic chains is still valuable, since they are the very chains, which are visible in simulation snapshots and cryo-TEM images. As a result, a natural question arises: What kind of chains should be taken into account? My reported results suggest that the chain definition should be chosen according to the phenomena one wants to describe. Even if the snapshots or cryo-TEM images show the presence of chains in a system, this is not the reason to conclude that all of those chains are kinetically stable and correlated enough to influence the macroscopic properties of the investigated ferrofluids.

After that I was interested in small angle neutron scattering (SANS) experiments. In these experiments one can obtain the structure factor, and I have developed a theoretical model to calculate the structure factor for the ferrofluid with strong interparticle magnetic dipole-dipole interactions for the range of ferroparticle densities, where the chain formation is observed for both mono- and bidisperse systems in the absence of an applied magnetic field [2]. The method is based on the explicit construction of radial distribution functions from the chain distributions obtained from DFT. The extensive comparison of the theoretical model and the

results of molecular dynamics simulation for a wide range of ferroparticle densities and coupling parameters has demonstrated a very good agreement for mono- and bidisperse systems. The height of the first maximum in the structure factor increases with both the dipolar coupling parameter and the density, which reflects the growth of clusters in the system and the increase of the simple combinatorial probability of finding two particles close to each other. It has been shown that the average distance between the particles in a chain plays an important role in theoretical description of the structure factor anisotropy and that its (distance) dependence on the coupling parameter has to be taken into account. In the limiting case of a small coupling parameter, the results of my model coincide with the predictions of the model recently developed by J.J. Cerda *et al.* [3] for spatially homogeneous (the coupling parameters are small to provide aggregation) ferrofluids. The interpretation of the scaling laws of the low-q region of the structure factor should be used with care, because the value of the scaling exponent D (i.e. the fractal dimension) becomes close to unity only with the largest values of the coupling parameter. Although the chain formation has been observed in all samples under study, the chain lengths are not sufficiently large to yield a scaling exponent close to unity. My investigation of bidisperse systems shows that the structure factor of a real bidisperse system is never the same as the structure factor of an ideal binary mixture. I have also shown that the scaling exponent D attains unity only in the absence of small particles and decreases with an increase in small particle density. These results show the demand for a proper description of polydispersity when dealing with real ferrofluids. The encouraging agreement found between the simulation data and the theory along with the set of facts supporting the theoretical assumptions makes me confident that the developed method can be used to analyze scattering images obtained experimentally from real ferrofluids, such as the recently investigated cobalt ferrofluids. They would fit perfectly the studied high coupling parameter and moderate particles concentration. The inherent polydispersity of these systems should not be an obstacle to the analysis, because the continuous particle size distribution can be approximated well by a bidisperse system. If the theoretical approach in the framework of the present study is successfully combined with molecular dynamic simulations, it provides the opportunity to deal with larger numbers of particle fractions. Moreover, my developed combined approach can help to reveal a direct relation between the experimental data for the SANS and microstructural observables, which is hardly possible using separately theory, experiments or simulations.

Now I am investigating the ferrofluids with anisotropic particles. They form the cutting edge of dipolar soft matter research as they correspond completely to the idea of fine tuning and designing new materials with controllable properties. As the first step, the analysis of possible ground state structures (the most energetically favored configurations at 0 K) for two and three dimensions was presented. For a system of magnetic ellipsoids in 2D with the magnetic moment along the short semi-axes, the ground state structure is similar to the system of magnetic spheres (an ideal ring and a chain). However, the critical number of particles (the number of particles for a ring to become the ground state, for dipolar spheres this critical number is 4) depends dramatically on the semi-axes ratio. The analysis of the interaction of two magnetic rods in 2D as a function of the semi-axes ratio is performed. With the semi-axes ratio less than a critical value (the diameter-to-height ratio, $z^* = 2^{-1/3}$), it was found that the anti-parallel orientation of the magnetic moments was energetically more advantageous, otherwise the head-to-tail orientation won. In a 3D case, the ground state of a system of elongated rods was investigated. I found two possible ground state structures (carpet and

bracelet), both of them with anti-parallel orientation of the magnetic moments. The carpet becomes an energetically favorable configuration for odd number of particles, and the bracelet is the ground state for even number of particles. In case of head-to-tail orientation of the magnetic moments, the ground state of a system of magnetic cylinders is similar to a system of magnetic ellipsoids with the magnetic moment along the short semi-axes.

According to this investigation, it is shown that the ground state structure depends not only on the number of particles (as for the system of magnetic spheres), but on the particle shape anisotropy. Even a slight shape anisotropy can lead to the drastic change in microstructure and, as a result, in macroscopic responses of the system. Depending on the asphericity of particles and their density, both the ground states and the equilibrium room temperature properties can be changed and effectively controlled.

REFERENCES

[1] C. Holm, A. Ivanov, S. Kantorovich, E. Pyanzina, E. Reznikov. Equilibrium properties of a bidisperse ferrofluid with chain aggregates: Theory and computer simulations. *Journal of Physics Condensed Matter.*, vol. 18 (2006), no. 38, pp. S2737–S2756.

[2] E. Pyanzina, S. Kantorovich, J.J. Cerda, A. Ivanov, C. Holm. How to analyse the structure factor in ferrofluids with strong magnetic interactions: A combined analytic and simulation approach. *Molecular Physics.*, vol. 107 (2009), no. 4-6, pp. 571–590.

[3] J.J. Cerda, E. Elfimova, V. Ballenegger, E. Krutikova, A. Ivanov, C. Holm. Study of the structure factor anisotropy and long range correlations of ferrofluids in the dilute low-coupling regime. *Journal of Magnetism and Magnetic Materials.*, vol. 323 (2011), no. 10, pp. 1246–1253.

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